Analysis of Pulse Discharge of a Lithium-Ion Battery

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During high rate discharges, steep gradients in concentrations develop resulting in discharge capacities much lower than the theoretical discharge capacity. It could be as low as 2% for a 30C (600 A/m^2) constant current discharge. However, under pulse discharge the obtained discharge capacity can be increased significantly. Further, high rate discharges are accompanied by large heat generations resulting in large temperature rises in the cell. This effect is alleviated by operating the cell under a pulsing current, in which case the cell cools down during the off time. Therefore, an analysis of pulse discharge becomes important in view of optimization of the pulse protocol as well as operating the cell safely.

The Li-ion system has been previously modeled and its behavior has been studied under constant current discharges. Doyle et al [1] developed a one-dimensional isothermal model of a $Li_xC_6/Li_yMn_2O_4$ system. They also validated the model by showing that the model predictions compare well with experimental data at low rates [2]. Fuller et al [3] used this model to study the phenomenon of relaxation in Li-ion systems, where in local concentrations inside the cell gradually become more uniform. Arora et al [4] and Botte et al [5] have extended this model to study the effect of side reactions. Thus, a theoretical study has not been conducted on pulse discharge of a Li-ion system. Secondly, most of the existing Li-ion battery models in literature describe the lithium intercalation process with a spherical diffusion equation characterized by a constant diffusion coefficient for lithium atoms in the electrode particles [1-6]. However, Verbrugge [7] and Botte et al [8] showed that it is important to include the state-of-charge dependence of diffusion coefficients in order to describe the system accurately. Verbrugge [7] also suggested a theoretical procedure to estimate the diffusion coefficient of lithium in carbon as a function of state-of-charge. In this work, the application of Verbrugge's method [7] to different Li-ion systems, in order to derive the state-of-charge dependence of the diffusion coefficients in the two electrodes, is described. This is then used in a one-dimensional nonisothermal model of a Li-ion system to predict cell behavior under pulse discharge. This model is developed by extending that presented by Doyle et al [1] to include energy balance and capacitance effects. The temperature and composition dependencies of transport properties (diffusion coefficients, conductivities and transference numbers) and kinetic properties (equilibrium exchange current densities) are incorporated. Variations of local temperature, potentials and concentrations with time and position inside a single cell sandwich are predicted using the model.

Figure 1a shows the predicted voltage-time response of a $Li_xC_6/Li_yMn_2O_4$ system for pulse discharge with an on time current density of 600 A/m^2. Also on the figure is the predicted voltage-time response for a constant current discharge at 600 A/m^2. It can be seen that pulsing results in much longer operation of the cell than discharging at constant current.

Figure 1b shows solution phase concentration profiles inside the cell at the end of one discharge and at the beginning of the next discharge (marked as points A and B in figure 1a). It can be seen that the steep concentration gradients inside the cell relax during the off time and become almost zero before the next discharge begins. Thus the cell can be discharged again until the concentration gradients become steep and this process could be repeated until the cell voltage after relaxation falls below the cut off.

The model is used for studying the relaxation effects and the performance of the cell under pulses of different amplitudes, duty cycles etc. Further, temperature rise inside the cell and its fall during rest periods are also analyzed. By this method one can achieve optimization of pulse protocols in order to maximize the delivered capacity and operate the cell safely.

References

1. M. Doyle, T. F. Fuller, and J. Newman, *J. Electrochem. Soc.*, **140**,1526 (1993).
2. M. Doyle, J. Newman, A. S. Gozdz, C. N. Schmutz, and J-M. Tarascon, *J. Electrochem. Soc.,* **143**, 1890 (1996).
3. T. F. Fuller, M. Doyle, and J. Newman, *J. Electrochem. Soc.*, **141**,982 (1994).
4. P. Arora, M. Doyle, R. E. White, *J. Electrochem. Soc.,* **146**, 3543 (1999).
5. G.G. Botte, B.A. Johnson, R. E. White, *J. Electrochem. Soc.,* **146**, 914 (1999).
6. P. Arora, M. Doyle, A. S. Gozdz, R.E. White, J. Newman, *J. Power Sources,* **88**, 219 (2000).
7. M.W. Verbrugge, B.J. Koch, *J. Electrochem. Soc.,* **143**, 600 (1996).
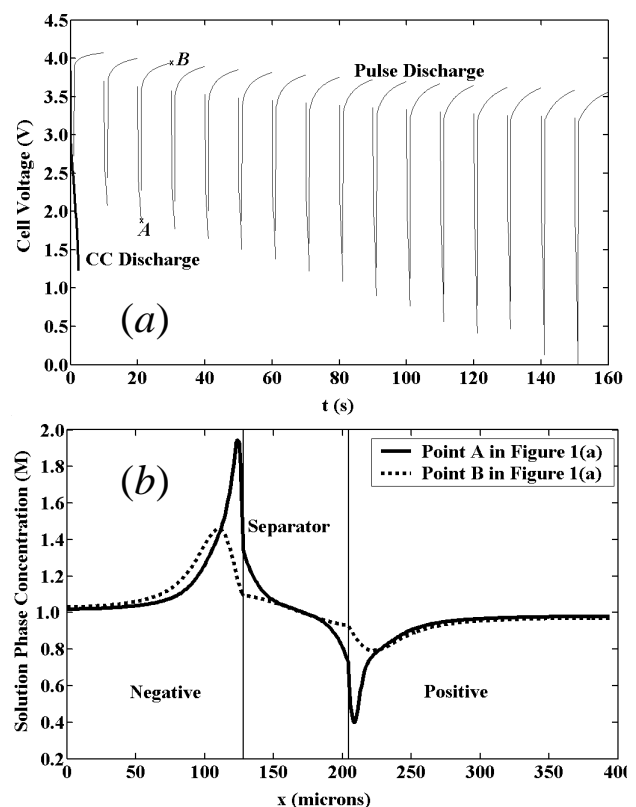8. G.G. Botte, R.E. White, *J. Electrochem. Soc.,* **148**, 54 (2001).

Figure 1. (a) Comparison between Constant Current and Pulse Discharge at 600 A/m^2. Constant Current discharge ends at about 2 s while pulsing results in a total on time of 16 s increasing the discharge capacity by 8 times. (b) Solution phase Li$^+$ Concentration profiles inside the cell at the beginning and end of the third off time designated by points A and B in (a).